

## PATENT ABSTRACTS OF JAPAN

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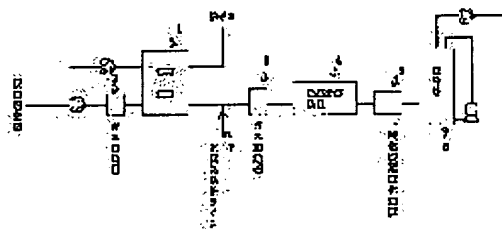
## (54) DEVICE FOR TREATING WASTE GAS CONTAINING ORGANIC HALOGEN COMPOUNDS

(57)Abstract:

PURPOSE: To effectively treat organic halogen compounds at low temperatures by installing a catalytic decomposition device packed with an organic halogen compound decomposition catalyst having a strong acidic point and a washing column for removing gaseous hydrogen halide generated by the decomposition of the organic halogen compounds.

CONSTITUTION: In a device where waste gas contg. organic halogen compounds (e.g. carbon tetrachloride) is treated and purified, a catalytic decomposition device 4 packed with an organic halogen compound decomposition catalyst having a strong scidic point (e.g. zeolite) and a washing column 6 for removing gaseous halogen halide generated by the decomposition of the organic halogen compounds are installed. And in the preceding stage of the catalytic decomposition device 4 are provided with a concentrator 1 and gas heaters 2, 3.

Further, in the poststage of the catalytic decomposition device 4 or the washing column 6, a carbon monoxide oxidizing device is provided, and in the prestage of the catalytic decomposition device 4, a steam feed line 7 is provided. And the organic halogen compound decomposition catalyst uses oxides of one or two or more of Si, Al, Ti, Zr, etc.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The processor of the exhaust gas containing the organic halogenated compound characterized by having the scrubbing tower which removes the catalyst cracking unit filled up with the organic halogenated compound decomposition catalyst which has a strong acid point in the equipment which processes and purifies the exhaust gas containing an organic halogenated compound, and the hydrogen halide gas which occurred by disassembly of an organic halogenated compound.

[Claim 2] The processor according to claim 1 characterized by forming concentration equipment in the preceding paragraph of a catalyst cracking unit.

[Claim 3] The processor according to claim 1 or 2 characterized by forming a gas heater in the preceding paragraph of a catalyst cracking unit.

[Claim 4] The processor according to claim 1 to 3 characterized by forming a carbon monoxide oxidation system after a catalyst cracking unit or a scrubbing tower.

[Claim 5] claim 1 characterized by preparing a steam supply line in front of a catalyst cracking unit - claim 4 -- a processor given in either.

[Claim 6] claim 1 characterized by organic halogenated compound decomposition catalysts being one sort or two sorts or more of oxides chosen from Si, aluminum, Ti, Zr, B, Nb, Cr, Ga, Mo, W, Y, Cu, Sr, La, Fe, Mn, and P - claim 5 -- a processor given in either.

[Claim 7] claim 1 to which an organic halogenated compound decomposition catalyst is characterized by supporting a sulfuric acid or phosphoric acid to an oxide according to claim 6 - claim 5 -- a processor given in either.

[Claim 8] claim 1 to which an organic halogenated compound decomposition catalyst is characterized by supporting one sort or two sorts or more of metals chosen as an oxide according to claim 6 or 7 from Cu, Fe, Co, nickel, Mn, Pt, Pd, Rh, Au, Ag, Ir, W, Mo, V, Cd, Sn, and Pb - claim 5 -- a processor given in either.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Industrial Application]** This invention relates to the processor of the exhaust gas containing an organic halogenated compound. Furthermore, after introducing the exhaust gas containing an organic halogenated compound into a catalyst cracking unit in detail and decomposing, it is related with the equipment from which the hydrogen halide which is the decomposition product of an organic halogenated compound in a scrubbing tower is removed.

**[0002]**

**[Description of the Prior Art]** The organic halogenated compound is used in various fields, such as not only the raw material of a chemical but a cleaning agent. The exhaust gas containing an organic halogenated compound is discharged in that case. However, the causative agent of what has toxicity, such as carcinogenic, or air pollution, the ozone layer depletion which poses a problem by earth environment further, and the thing considered as a causative agent of greenhouse effect are also in these organic halogenated compounds, and development of a discharge control technique is furthered.

**[0003]** As a processor of the exhaust gas containing an organic halogenated compound, the adsorption collecting method is learned conventionally. However, by the adsorption collecting method, processing of the collected organic halogenated compound poses a problem. The impurity is usually being mixed in many cases, and before reusing, it is necessary for direct reuse to be possible when it is a recovery object with high purity, but to carry out distillation purification. Moreover, it is necessary to process as waste fluid what is not reusable in a recovery object, and it also has the problem that the cost for it starts.

**[0004]** In addition to the adsorption collecting method, a direct combustion method is also considered as an art. However, the temperature of 800 degrees C or more is required for a direct combustion method, and the temperature of 1000 degrees C or more is needed depending on the class of organic halogenated compound. Moreover, in order to carry out at an elevated temperature, thermal NOx occurs, dioxin may generate a direct combustion method further, and it causes a new pollution problem.

**[0005]**

**[Problem(s) to be Solved by the Invention]** As mentioned above, the art of the exhaust gas containing an organic halogenated compound has a problem in after treatment, and also has a possibility of becoming the cause of a new pollution problem, and development of the processor of the exhaust gas containing a more effective organic halogenated compound is desired.

**[0006]** After condensing an organic halogenated compound with concentration equipment when an organic halogenated compound is low concentration as a result of this invention persons' examining the art of the exhaust gas containing an organic halogenated compound, by introducing into a catalyst cracking unit directly in a high-concentration case, and removing hydrogen halide by the scrubbing tower after that, it succeeded in processing the exhaust gas which contains an organic halogenated compound efficiently by whenever [ low-temperature ], and the processor of this invention was completed.

**[0007]**

**[Means for Solving the Problem]** The processor of the exhaust gas containing the organic halogenated compound characterized by this invention consisting of a scrubbing tower which removes the hydrogen halide generated by disassembly of the catalyst cracking unit filled up with the organic halogen decomposition catalyst which has a strong acid point, and an organic halogenated compound is offered.

**[0008]** Next, this invention is explained in full detail.

**[0009]** The organic halogenated compound set as the object of processing by this invention is a compound containing at

least one sort in chlorine, a fluorine, and a bromine, and a carbon tetrachloride, chloroform, chloroethylene, 1,1,1-trichloroethane, 1,2-dichloroethane, tetrachloroethylene, a trichloroethylene, chloroethylene, dichloromethane, trichlorofluoromethane, a dichlorodifluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, a methyl bromide, etc. are raised as an example.

[0010] When the organic halogenated compound in exhaust gas is low concentration, an organic halogenated compound is condensed using concentration equipment, and it introduces into a catalyst cracking unit. Concentration to be condensed is 1000 ppm or less preferably, and is 500 ppm or less still more preferably. It is especially possible to use common honeycomb rotor mold concentration equipment, a restoration mold adsorber, etc. as concentration equipment, and it is not restricted. Moreover, granular active carbon, fibrous activated carbon, the zeolite of the adsorbent used for concentration equipment, etc. are [ all ] usable.

[0011] The organic halogenated compound condensed by concentration equipment is introduced into a catalyst cracking unit.

[0012] the approach the approach to which temperature required for catalyst decomposition is applied in a catalyst cracking unit heats gas before being introduced into a catalyst cracking unit, or a catalyst -- a column -- the approach of heating the very thing can be used. Direct heating according [ the approach of heating gas before being introduced into catalyst equipment ] to an electric heater, a combustion burner, a high-pressure steam, etc., and indirect heating are used. However, in the case of an inflammable high-concentration organic halogenated compound, since there is danger of explosion, indirect heating is desirable. moreover, the method of heating a catalyst bed directly -- a catalyst -- the method of heating the outer wall of a column by the electric heater and the combustion burner or the approach of embedding an electric heater into a catalyst bed, the approach of embedding tubing which let the gas heated by the combustion burner etc. pass into a catalyst bed, etc. are used. Moreover, as for the quality of the material of a catalyst splitting column, it is desirable to use the acid-proof quality of the materials, such as nickel, Inconel, a nickel-Cr alloy, an acid-proof metal of SUS310S grade or ceramic coating, and glass lining.

[0013] the catalyst of a catalyst cracking unit -- especially the mold of a column is not limited but its various gestalten, such as a restoration mold, a radian flow molds, and a monolith type, are usable.

[0014] The organic halogen decomposition catalyst used by this invention has a super-strong acid point, it is one sort or two sorts or more of oxide chosen from Si, aluminum, Ti, Zr, B, Nb, Cr, Ga, Mo, W, Y, Cu, Sr, La, Fe, Mn, and P, and a zeolite, silica alumina, a silica titania, a titania zirconia, alumina boria, niobium oxide, etc. are raised as an example. Moreover, the sulfuric acid and phosphoric acid which are an acid of a non-volatile may be supported to these oxides, and a super-strong acid point may be made to increase to them.

[0015] Since poisoning may be carried out to a halogen, it is [ an above catalyst independent ] required in noble metals, transition metals, etc. the ion exchange or to make it support and for such a catalyst to give the endurance to a halogen. Furthermore, it is also expectable that catalytic activity goes up noble metals and transition metals the ion exchange or by supporting.

[0016] As a metal to embellish, Cu, Fe, Co, nickel, Mn, Pt, Pd, Rh, Au, Ag, Ir, W, Mo, V, Cd, Sn, and Pb are raised, and these one sort or two sorts or more are used. The ion exchange or 0.05 - 20wt% of the amount of qualification metals to support is desirable.

[0017] These organic halogenated compound decomposition catalysts are solid acid catalysts which have a strong acid point. When helium gas is measured by the rate of flow of 10 ml/min and the temperature programmed desorption of a pyridine is measured with the programming rate of 10 degrees C / min with a sink as carrier gas after the strong acid point in this invention made the pyridine stick to a catalyst at 300 degrees C, it is an acid site from which a pyridine is desorbed at the temperature of 600 degrees C or more. Moreover, either a Broensted acid point or a Lewis acid point is OK as the class of acid site of a solid acid catalyst.

[0018] When the example of an organic halogen decomposition catalyst is given, Co support H mold mordenite, Fe support H mold mordenite, W support titania zirconia multiple oxide, Pd support titania zirconia multiple oxide, Cr support titania zirconia multiple oxide, Pt support alumina boria multiple oxide, Pt support niobium oxide, etc. are \*\*.

[0019] the use gestalt of a catalyst -- the shape of the shape of a honeycomb, a globular shape, a column, and sheet metal, and reticulated \*\* -- although various gestalten are usable, when the amount of raw gas is large, the shape of a honeycomb with few pressure losses is desirable. Moreover, although decomposition temperature changes with organic halogenated compounds, it is 150-450 degrees C preferably 100-600 degrees C.

[0020] It is necessary to add a steam depending on the class of organic halogenated compound in the case of catalyst decomposition. For example, the compound which does not contain a hydrogen atom like par halocarbon is difficult for catalyst oxidative degradation, and needs an elevated temperature. However, it is easily decomposed by adding a steam. In the case of a carbon tetrachloride, by oxidative degradation, the temperature of 600 degrees C or more is needed, but

hydrolysis by addition of a steam can decompose 100% at the temperature of 200 degrees C.

[0021] Moreover, in disassembly of an organic halogenated compound, the halogen gas which halogen gas occurred in many cases and occurred in the oxidative degradation by oxygen is more difficult to remove than hydrogen halide. However, by adding a steam, hydrogen halide can be made to generate preferentially and water and an alkali water solution can remove easily. Thus, making a steam exist in reactant gas has many advantages. The oxygen to add and a water vapor content should just be the amounts of theory of 1.5 times or more preferably that what is necessary is just an amount more than the amount of theory which converts into a carbon dioxide and hydrogen halide the carbon atom contained in an organic halogenated compound, and a halogen atom. For example, in the case of the gas containing 1000 ppm of carbon tetrachlorides, what is necessary is just 1500 ppm or more of oxygen, and 3000 ppm or more of steams preferably that the oxygen added should be 1000 ppm or more, and a steam should just be 2000 ppm or more.

[0022] As for the gas decomposed with the catalyst cracking unit, it is desirable to carry out heat exchange to the gas before decomposition by the heat exchanger, and it is useful to laborsaving of the heating energy of gas. Since hydrogen halide is contained in gas, acid-proof things of the quality of the material of a heat exchanger, such as acid-proof metal, a product made from the ceramics, or a product made from glass lining, are desirable.

[0023] The gas decomposed with the catalyst cracking unit is introduced into a scrubbing tower, and the hydrogen halide which is the decomposition product of an organic halogenated compound is removed by water or the alkali water solution.

[0024] a scrubbing tower -- a column -- the general method of establishing water or an alkali water solution in a sink and the lower part from the upper part, and establishing a gas outlet in a gas entry and the upper part is desirable. Moreover, the interior of a scrubbing tower is filled up with the bulking agent, and the method of taking the large liquid contact area of gas is desirable. Since a bulking agent has a possibility of hydrogen halide dissolving and becoming aqueous acids, its bulking agent made from the product made from plastics and the ceramics is desirable. Although there are an approach of discharging as it is after washing and the approach of circulating through and using it with a pump, its latter is desirable, when using water as a penetrant remover and a penetrant remover uses the former and an alkali water solution as a penetrant remover. Since acidity goes up and absorption efficiency worsens by the absorbed hydrogen halide when circulating through and using a penetrant remover, it is desirable to perform actuation which adds alkali moderately, maintains pH of a penetrant remover, further always discharges some penetrant removers, and is replaced with a new penetrant remover. Although the halogen ion of chlorine, a fluorine, and a bromine is contained in wastewater liquid, since the concentration which can be discharged by effluent control is decided, it is necessary in these to remove a fluorine. There is a method of contacting the matter which forms an insoluble salt in response to a penetrant remover to a fluorine as an approach of removing fluorine ion etc. For example, by contacting a penetrant remover to a calcium chloride, an insoluble calcium fluoride is built in water and it can collect as settlings.

[0025] In this decomposition reaction, a \*\*\*\*\* case has a carbon monoxide according to the class of organic halogenated compound, and the class of organic halogenated compound decomposition catalyst. Since the carbon monoxide is harmful, it is necessary to process it by a certain approach. In this invention, the approach of changing a carbon monoxide into a carbon dioxide using an oxidation catalyst is used. A limit is not carried out that things of an oxidation catalyst currently generally used, such as Pt-alumina, Pd-alumina, Pt-titania, Pd-titania, Pt-titania zirconia multiple oxide, and Pd-titania zirconia multiple oxide, are usable and specially. A carbon monoxide oxidation catalyst may be used, mixing with an organic halogenated compound decomposition catalyst, and may be installed immediately after a catalyst cracking unit and after a scrubbing tower as a carbon monoxide oxidation system. When using it, mixing with an organic halogenated compound decomposition catalyst, and when installing immediately after a catalyst cracking unit, in order to react with the heated gas, there is newly no need for heating of gas, and it is not necessary to use excessive energy. However, since hydrogen halide exists in gas in these cases, as for a catalyst, it is desirable to use the catalyst of the titania system by which poisoning cannot be easily carried out to a halogen. Moreover, when installing after a scrubbing tower, since a halogen hardly exists, there are no worries about poisoning of a catalyst, but since the temperature of gas is falling to near the room temperature, it is necessary to heat to temperature required for a reaction. As for the reheated gas, it is desirable to collect heat through a heat exchanger.

[0026]

[Effect of the Invention] Processing of the organic halogenated compound currently conventionally emitted into atmospheric air as it was as exhaust gas about the environmental purification which poses a current problem is possible for this invention.

[0027]

[Example] Although an example is shown below, this invention is not limited to these.

[0028] The gas (other components: dry air) containing examples 11 and 1 and 1-trichloroethane 60ppm and 2% of

streams was prepared, and it considered as processed gas.

[0029] Using concentration equipment (1) as honeycomb rotor mold concentration equipment, the rotor part used the honeycomb mold activated carbon fiber with a diameter [ of 60cm ], and a die length of 40cm.

[0030] an organic halogenated compound decomposition catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Cr -- 5wt(s)% -- it supported and what was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm was used. moreover, a carbon monoxide oxidation catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Pd -- 1wt% -- what supported what was supported to the honeycomb (2mm of openings) of cordierite with a diameter [ of 30cm ] and a die length of 40cm was used.

[0031] Processed gas was introduced into concentration equipment (1) by 1500m<sup>3</sup>/Hr, and operated the rotational frequency of a rotor as 6rph(s).

[0032] The air for desorption (a steam is included 2%) was introduced into the desorption section of a rotor by flow rate of 150m<sup>3</sup>/Hr after heating at 150 degrees C with the gas heater for concentration equipments (2).

[0033] The steam was supplied from the steam supply line (7) so that it might become 2wt(s)% in this desorption gas about a steam, and it introduced into the catalyst cracking unit (4) after heating at 400 degrees C with the gas heater for catalyst cracking units (3). What put the above-mentioned catalyst in the container with a diameter [ of 55cm ] and a die length of 70cm was used for the catalyst cracking unit (4). After the gas which came out of the catalyst cracking unit (4) was introduced into the carbon monoxide oxidation system (5) in which the above-mentioned carbon monoxide oxidation catalyst was put and oxidized the carbon monoxide, it was introduced into the scrubbing tower (6) and washed by the NaOH water solution 5%.

[0034] The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chlorides, and 1,1,1-trichloroethane, chlorine gas, and a carbon monoxide were not contained.

[0035] as an example 2 organic halogenated compound -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Pd -- 1wt% -- it carried out by the same approach as an example 1 except having supported, having used what was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm, and having not used a carbon monoxide oxidation catalyst. The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chlorides, and 1,1,1-trichloroethane, chlorine gas, and a carbon monoxide were not contained.

[0036] It supports. as an example 3 organic halogenated compound -- a carbon tetrachloride -- using it -- as an organic halogenated compound decomposition catalyst -- H mold mordenite (TOSOH CORP. make HSZ-620HOA) -- Co -- 2wt(s)% -- as a binder -- an alumina -- 20wt(s)% -- what was used and was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm was used, whenever [ gas stoving temperature ] was made into 220 degrees C, and it carried out by the same approach as an example 2 except having not used a carbon monoxide oxidation catalyst.

[0037] The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chlorides, and a carbon tetrachloride, chlorine gas, and a carbon monoxide were not contained.

[0038] as an example 4 organic halogenated compound -- 1, 1, 2-TORIKUROROH 1 and 2, and 2-trifluoro ethane -- using it -- as an organic halogenated compound decomposition catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- W -- 2wt(s)% -- it supported and carried out by the same approach as an example 1 except having used what was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm.

[0039] A hydrogen chloride and the hydrogen fluoride of the presentation of the exhaust gas after washing are 1 ppm or less, and 1, 1, 2-TORIKUROROH 1 and 2, 2-trifluoro ethane, chlorine gas, fluorine gas, and a carbon monoxide were not contained.

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TECHNICAL FIELD

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[Industrial Application] This invention relates to the processor of the exhaust gas containing an organic halogenated compound. Furthermore, after introducing the exhaust gas containing an organic halogenated compound into a catalyst cracking unit in detail and decomposing, it is related with the equipment from which the hydrogen halide which is the decomposition product of an organic halogenated compound in a scrubbing tower is removed.

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**PRIOR ART**

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[Description of the Prior Art] The organic halogenated compound is used in various fields, such as not only the raw material of a chemical but a cleaning agent. The exhaust gas containing an organic halogenated compound is discharged in that case. However, the causative agent of what has toxicity, such as carcinogenic, or air pollution, the ozone layer depletion which poses a problem by earth environment further, and the thing considered as a causative agent of greenhouse effect are also in these organic halogenated compounds, and development of a discharge control technique is furthered.

[0003] As a processor of the exhaust gas containing an organic halogenated compound, the adsorption collecting method is learned conventionally. However, by the adsorption collecting method, processing of the collected organic halogenated compound poses a problem. The impurity is usually being mixed in many cases, and before reusing, it is necessary for direct reuse to be possible when it is a recovery object with high purity, but to carry out distillation purification. Moreover, it is necessary to process as waste fluid what is not reusable in a recovery object, and it also has the problem that the cost for it starts.

[0004] In addition to the adsorption collecting method, a direct combustion method is also considered as an art. However, the temperature of 800 degrees C or more is required for a direct combustion method, and the temperature of 1000 degrees C or more is needed depending on the class of organic halogenated compound. Moreover, in order to carry out at an elevated temperature, thermal NOx occurs, dioxin may generate a direct combustion method further, and it causes a new pollution problem.

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EFFECT OF THE INVENTION

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[Effect of the Invention] Processing of the organic halogenated compound currently conventionally emitted into atmospheric air as it was as exhaust gas about the environmental purification which poses a current problem is possible for this invention.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] As mentioned above, the art of the exhaust gas containing an organic halogenated compound has a problem in after treatment, and also has a possibility of becoming the cause of a new pollution problem, and development of the processor of the exhaust gas containing a more effective organic halogenated compound is desired.

[0006] After condensing an organic halogenated compound with concentration equipment when an organic halogenated compound is low concentration as a result of this invention persons' examining the art of the exhaust gas containing an organic halogenated compound, by introducing into a catalyst cracking unit directly in a high-concentration case, and removing hydrogen halide by the scrubbing tower after that, it succeeded in processing the exhaust gas which contains an organic halogenated compound efficiently by whenever [ low-temperature ], and the processor of this invention was completed.

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**MEANS**

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[Means for Solving the Problem] The processor of the exhaust gas containing the organic halogenated compound characterized by this invention consisting of a scrubbing tower which removes the hydrogen halide generated by disassembly of the catalyst cracking unit filled up with the organic halogen decomposition catalyst which has a strong acid point, and an organic halogenated compound is offered.

[0008] Next, this invention is explained in full detail.

[0009] The organic halogenated compound set as the object of processing by this invention is a compound containing at least one sort in chlorine, a fluorine, and a bromine, and a carbon tetrachloride, chloroform, chloroethylene, 1,1,1-trichloroethane, 1,2-dichloroethane, tetrachloroethylene, a trichloroethylene, chloroethylene, dichloromethane, trichlorofluoromethane, a dichlorodifluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane, a methyl bromide, etc. are raised as an example.

[0010] When the organic halogenated compound in exhaust gas is low concentration, an organic halogenated compound is condensed using concentration equipment, and it introduces into a catalyst cracking unit. Concentration to be condensed is 1000 ppm or less preferably, and is 500 ppm or less still more preferably. It is especially possible to use common honeycomb rotor mold concentration equipment, a restoration mold adsorber, etc. as concentration equipment, and it is not restricted. Moreover, granular active carbon, fibrous activated carbon, the zeolite of the adsorbent used for concentration equipment, etc. are [ all ] usable.

[0011] The organic halogenated compound condensed by concentration equipment is introduced into a catalyst cracking unit.

[0012] the approach the approach to which temperature required for catalyst decomposition is applied in a catalyst cracking unit heats gas before being introduced into a catalyst cracking unit, or a catalyst -- a column -- the approach of heating the very thing can be used. Direct heating according [ the approach of heating gas before being introduced into catalyst equipment ] to an electric heater, a combustion burner, a high-pressure steam, etc., and indirect heating are used. However, in the case of an inflammable high-concentration organic halogenated compound, since there is danger of explosion, indirect heating is desirable. moreover, the method of heating a catalyst bed directly -- a catalyst -- the method of heating the outer wall of a column by the electric heater and the combustion burner or the approach of embedding an electric heater into a catalyst bed, the approach of embedding tubing which let the gas heated by the combustion burner etc. pass into a catalyst bed, etc. are used. Moreover, as for the quality of the material of a catalyst splitting column, it is desirable to use the acid-proof quality of the materials, such as nickel, Inconel, a nickel-Cr alloy, an acid-proof metal of SUS310S grade or ceramic coating, and glass lining.

[0013] the catalyst of a catalyst cracking unit -- especially the mold of a column is not limited but its various gestalten, such as a restoration mold, a radian flow molds, and a monolith type, are usable.

[0014] The organic halogen decomposition catalyst used by this invention has a super-strong acid point, it is one sort or two sorts or more of oxide chosen from Si, aluminum, Ti, Zr, B, Nb, Cr, Ga, Mo, W, Y, Cu, Sr, La, Fe, Mn, and P, and a zeolite, silica alumina, a silica titania, a titania zirconia, alumina boria, niobium oxide, etc. are raised as an example. Moreover, the sulfuric acid and phosphoric acid which are an acid of a non-volatile may be supported to these oxides, and a super-strong acid point may be made to increase to them.

[0015] Since poisoning may be carried out to a halogen, it is [ an above catalyst independent ] required in noble metals, transition metals, etc. the ion exchange or to make it support and for such a catalyst to give the endurance to a halogen. Furthermore, it is also expectable that catalytic activity goes up noble metals and transition metals the ion exchange or by supporting.

[0016] As a metal to embellish, Cu, Fe, Co, nickel, Mn, Pt, Pd, Rh, Au, Ag, Ir, W, Mo, V, Cd, Sn, and Pb are raised, and these one sort or two sorts or more are used. The ion exchange or 0.05 - 20wt% of the amount of qualification

metals to support is desirable.

[0017] These organic halogenated compound decomposition catalysts are solid acid catalysts which have a strong acid point. When helium gas is measured by the rate of flow of 10 ml/min and the temperature programmed desorption of a pyridine is measured with the programming rate of 10 degrees C / min with a sink as carrier gas after the strong acid point in this invention made the pyridine stick to a catalyst at 300 degrees C, it is an acid site from which a pyridine is desorbed at the temperature of 600 degrees C or more. Moreover, either a Broensted acid point or a Lewis acid point is OK as the class of acid site of a solid acid catalyst.

[0018] When the example of an organic halogen decomposition catalyst is given, Co support H mold mordenite, Fe support H mold mordenite, W support titania zirconia multiple oxide, Pd support titania zirconia multiple oxide, Cr support titania zirconia multiple oxide, Pt support alumina boria multiple oxide, Pt support niobium oxide, etc. are \*\*.

[0019] the use gestalt of a catalyst -- the shape of the shape of a honeycomb, a globular shape, a column, and sheet metal, and reticulated \*\* -- although various gestalten are usable, when the amount of raw gas is large, the shape of a honeycomb with few pressure losses is desirable. Moreover, although decomposition temperature changes with organic halogenated compounds, it is 150-450 degrees C preferably 100-600 degrees C.

[0020] It is necessary to add a steam depending on the class of organic halogenated compound in the case of catalyst decomposition. For example, the compound which does not contain a hydrogen atom like par halocarbon is difficult for catalyst oxidative degradation, and needs an elevated temperature. However, it is easily decomposed by adding a steam. In the case of a carbon tetrachloride, by oxidative degradation, the temperature of 600 degrees C or more is needed, but hydrolysis by addition of a steam can decompose 100% at the temperature of 200 degrees C.

[0021] Moreover, in disassembly of an organic halogenated compound, the halogen gas which halogen gas occurred in many cases and occurred in the oxidative degradation by oxygen is more difficult to remove than hydrogen halide. However, by adding a steam, hydrogen halide can be made to generate preferentially and water and an alkali water solution can remove easily. Thus, making a steam exist in reactant gas has many advantages. The oxygen to add and a water vapor content should just be the amounts of theory of 1.5 times or more preferably that what is necessary is just an amount more than the amount of theory which converts into a carbon dioxide and hydrogen halide the carbon atom contained in an organic halogenated compound, and a halogen atom. For example, in the case of the gas containing 1000 ppm of carbon tetrachlorides, what is necessary is just 1500 ppm or more of oxygen, and 3000 ppm or more of steams preferably that the oxygen added should be 1000 ppm or more, and a steam should just be 2000 ppm or more.

[0022] As for the gas decomposed with the catalyst cracking unit, it is desirable to carry out heat exchange to the gas before decomposition by the heat exchanger, and it is useful to laborsaving of the heating energy of gas. Since hydrogen halide is contained in gas, acid-proof things of the quality of the material of a heat exchanger, such as acid-proof metal, a product made from the ceramics, or a product made from glass lining, are desirable.

[0023] The gas decomposed with the catalyst cracking unit is introduced into a scrubbing tower, and the hydrogen halide which is the decomposition product of an organic halogenated compound is removed by water or the alkali water solution.

[0024] a scrubbing tower -- a column -- the general method of establishing water or an alkali water solution in a sink and the lower part from the upper part, and establishing a gas outlet in a gas entry and the upper part is desirable. Moreover, the interior of a scrubbing tower is filled up with the bulking agent, and the method of taking the large liquid contact area of gas is desirable. Since a bulking agent has a possibility of hydrogen halide dissolving and becoming aqueous acids, its bulking agent made from the product made from plastics and the ceramics is desirable. Although there are an approach of discharging as it is after washing and the approach of circulating through and using it with a pump, its latter is desirable, when using water as a penetrant remover and a penetrant remover uses the former and an alkali water solution as a penetrant remover. Since acidity goes up and absorption efficiency worsens by the absorbed hydrogen halide when circulating through and using a penetrant remover, it is desirable to perform actuation which adds alkali moderately, maintains pH of a penetrant remover, further always discharges some penetrant removers, and is replaced with a new penetrant remover. Although the halogen ion of chlorine, a fluorine, and a bromine is contained in wastewater liquid, since the concentration which can be discharged by effluent control is decided, it is necessary in these to remove a fluorine. There is a method of contacting the matter which forms an insoluble salt in response to a penetrant remover to a fluorine as an approach of removing fluorine ion etc. For example, by contacting a penetrant remover to a calcium chloride, an insoluble calcium fluoride is built in water and it can collect as settlings.

[0025] In this decomposition reaction, a \*\*\*\*\* case has a carbon monoxide according to the class of organic halogenated compound, and the class of organic halogenated compound decomposition catalyst. Since the carbon monoxide is harmful, it is necessary to process it by a certain approach. In this invention, the approach of changing a carbon monoxide into a carbon dioxide using an oxidation catalyst is used. A limit is not carried out that things of an

oxidation catalyst currently generally used, such as Pt-alumina, Pd-alumina, Pt-titania, Pd-titania, Pt-titania zirconia multiple oxide, and Pd-titania zirconia multiple oxide, are usable and specially. A carbon monoxide oxidation catalyst may be used, mixing with an organic halogenated compound decomposition catalyst, and may be installed immediately after a catalyst cracking unit and after a scrubbing tower as a carbon monoxide oxidation system. When using it, mixing with an organic halogenated compound decomposition catalyst, and when installing immediately after a catalyst cracking unit, in order to react with the heated gas, there is newly no need for heating of gas, and it is not necessary to use excessive energy. However, since hydrogen halide exists in gas in these cases, as for a catalyst, it is desirable to use the catalyst of the titania system by which poisoning cannot be easily carried out to a halogen. Moreover, when installing after a scrubbing tower, since a halogen hardly exists, there are no worries about poisoning of a catalyst, but since the temperature of gas is falling to near the room temperature, it is necessary to heat to temperature required for a reaction. As for the reheated gas, it is desirable to collect heat through a heat exchanger.

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EXAMPLE

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[Example] Although an example is shown below, this invention is not limited to these.

[0028] The gas (other components: dry air) containing examples 11 and 1 and 1-trichloroethane 60ppm and 2% of steams was prepared, and it considered as processed gas.

[0029] Using concentration equipment (1) as honeycomb rotor mold concentration equipment, the rotor part used the honeycomb mold activated carbon fiber with a diameter [ of 60cm ], and a die length of 40cm.

[0030] an organic halogenated compound decomposition catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Cr -- 5wt(s)% -- it supported and what was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm was used. moreover, a carbon monoxide oxidation catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Pd -- 1wt% -- what supported what was supported to the honeycomb (2mm of openings) of cordierite with a diameter [ of 30cm ] and a die length of 40cm was used.

[0031] Processed gas was introduced into concentration equipment (1) by 1500m<sup>3</sup>/Hr, and operated the rotational frequency of a rotor as 6rph(s).

[0032] The air for desorption (a steam is included 2%) was introduced into the desorption section of a rotor by flow rate of 150m<sup>3</sup>/Hr after heating at 150 degrees C with the gas heater for concentration equipments (2).

[0033] The steam was supplied from the steam supply line (7) so that it might become 2wt(s)% in this desorption gas about a steam, and it introduced into the catalyst cracking unit (4) after heating at 400 degrees C with the gas heater for catalyst cracking units (3). What put the above-mentioned catalyst in the container with a diameter [ of 55cm ] and a die length of 70cm was used for the catalyst cracking unit (4). After the gas which came out of the catalyst cracking unit (4) was introduced into the carbon monoxide oxidation system (5) in which the above-mentioned carbon monoxide oxidation catalyst was put and oxidized the carbon monoxide, it was introduced into the scrubbing tower (6) and washed by the NaOH water solution 5%.

[0034] The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chlorides, and 1,1,1-trichloroethane, chlorine gas, and a carbon monoxide were not contained.

[0035] as an example 2 organic halogenated compound -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- Pd -- 1wt% -- it carried out by the same approach as an example 1 except having supported, having used what was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm, and having not used a carbon monoxide oxidation catalyst. The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chlorides, and 1,1,1-trichloroethane, chlorine gas, and a carbon monoxide were not contained.

[0036] It supports. as an example 3 organic halogenated compound -- a carbon tetrachloride -- using it -- as an organic halogenated compound decomposition catalyst -- H mold mordenite (TOSOH CORP. make HSZ-620HOA) -- Co -- 2wt(s)% -- as a binder -- an alumina -- 20wt(s)% -- what was used and was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm was used, whenever [ gas stoving temperature ] was made into 220 degrees C, and it carried out by the same approach as an example 2 except having not used a carbon monoxide oxidation catalyst.

[0037] The presentation of the exhaust gas after washing is 1 ppm or less of hydrogen chlorides, and a carbon tetrachloride, chlorine gas, and a carbon monoxide were not contained.

[0038] as an example 4 organic halogenated compound -- 1, 1, 2-TORIKUROROH 1 and 2, and 2-trifluoro ethane -- using it -- as an organic halogenated compound decomposition catalyst -- a titania zirconia multiple oxide (Ti/Zr=1.4) -- W -- 2wt(s)% -- it supported and carried out by the same approach as an example 1 except having used what was fabricated on the pellet of diameter 1.5mmphi and the shape of a cylinder with a die length of 5mm.

[0039] A hydrogen chloride and the hydrogen fluoride of the presentation of the exhaust gas after washing are 1 ppm or less, and 1, 1, 2-TORIKUROROH 1 and 2, 2-trifluoro ethane, chlorine gas, fluorine gas, and a carbon monoxide were

not contained.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is one example of the flow sheet of the equipment of this invention.

[Description of Notations]

- 1 -- Concentration equipment
- 2 -- Gas heater for concentration equipments
- 3 -- Gas heater for catalyst cracking units
- 4 -- Catalyst cracking unit
- 5 -- Carbon monoxide cracking unit
- 6 -- Scrubbing tower
- 7 -- Steam supply line

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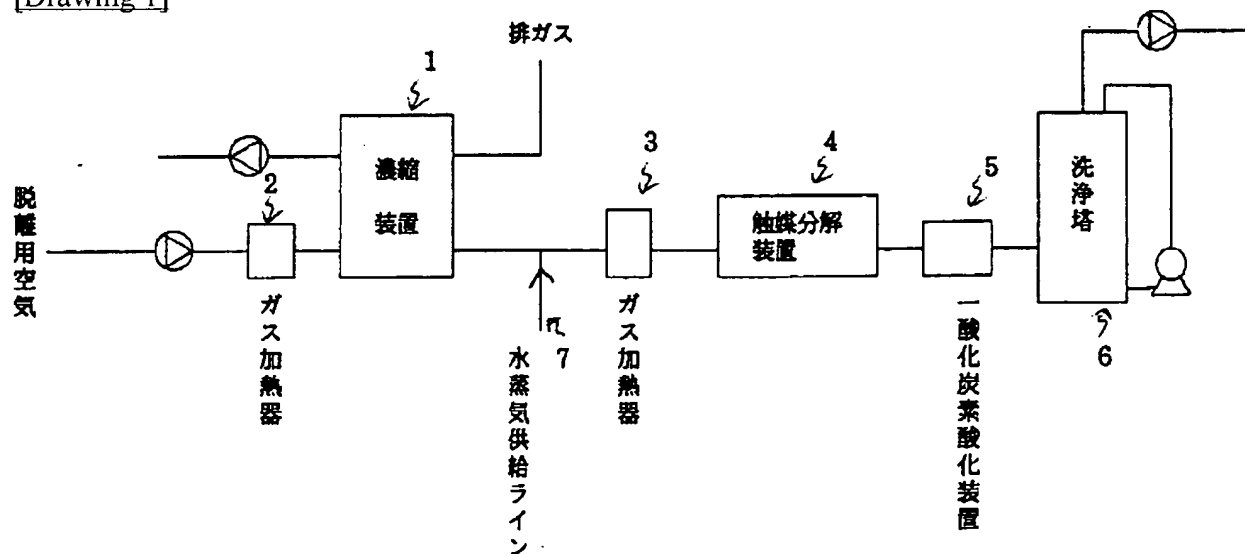
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## DRAWINGS

[Drawing 1]



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